Liquid-liquid equilibriums in aqueous solutions of demixing amines loaded with gas for CO 2 capture processes

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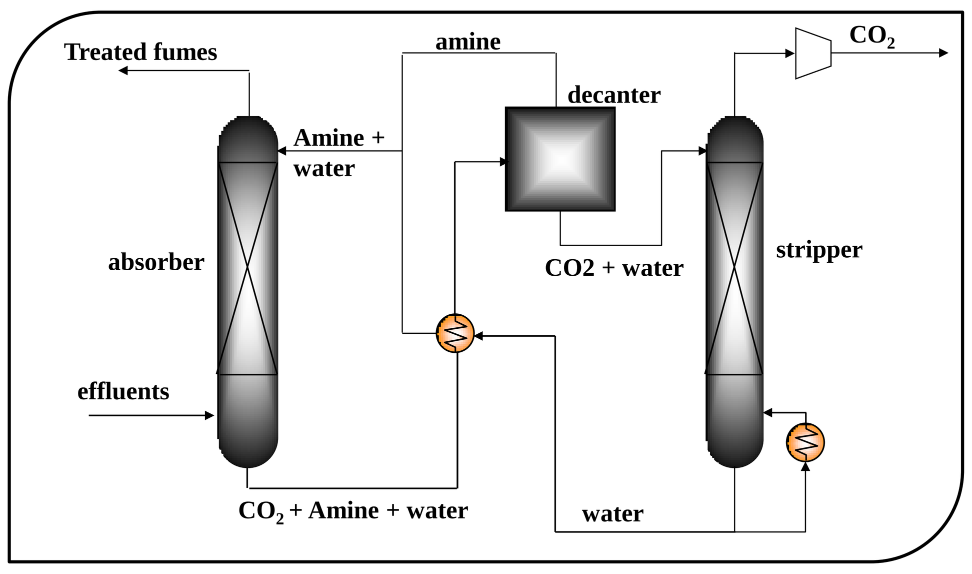
Introduction

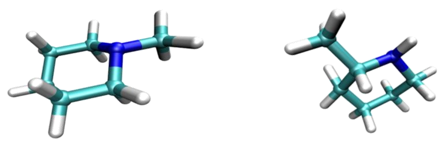


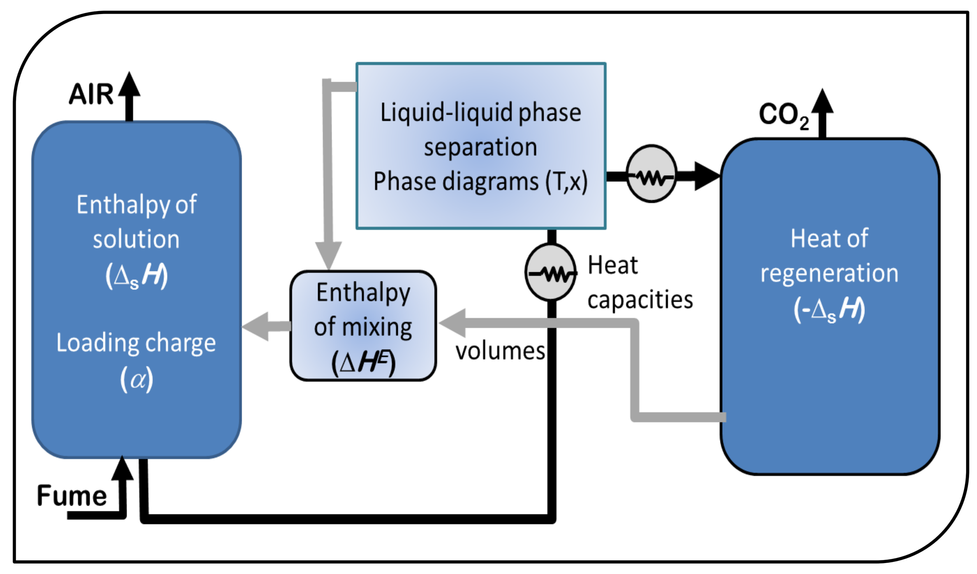
Aqueous solutions of amines are selective carbon dioxide (CO_2) absorbents [1,2] . They are used in CO_2 capture processes working on absorption/desorption cycles.

Demixing amines may be valuable for new capture processes [3].
These amines demonstrate a liquid-liquid phase separation [4] which can be used to reduce energy costs of desorption (absorbent regeneration).

Aim of this paper : presentation of a method developed in the laboratory to study precisely the LLE in the binary solutions water + amines and the ternary mixtures water+amine+CO_2, as a function of the pressure and the CO_2 loading charge.

Amines : N-methylpiperidine
2-methylpiperidine

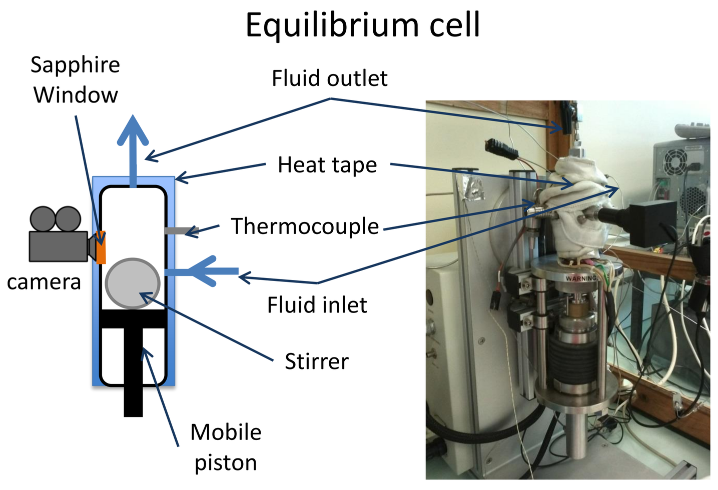




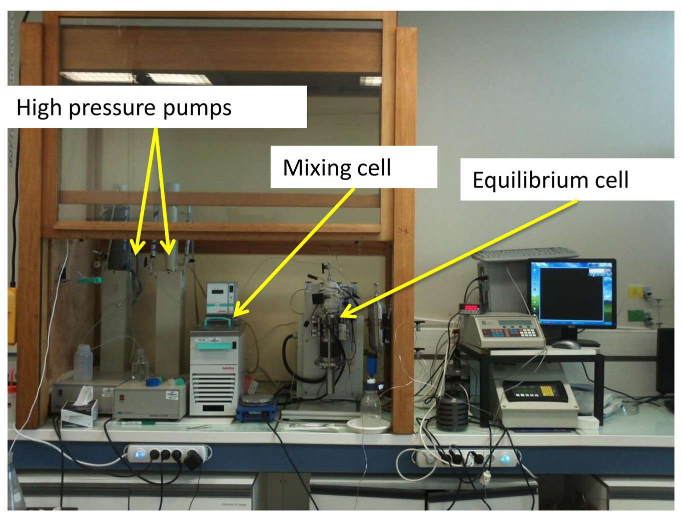
methods

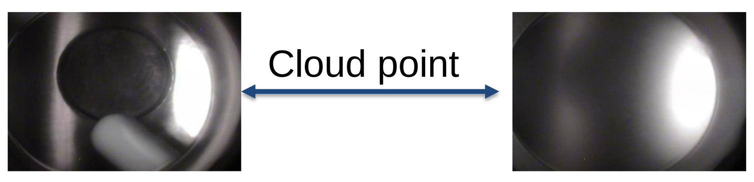
Hastelloy cell : THAR SPM20

Equilibrium cell



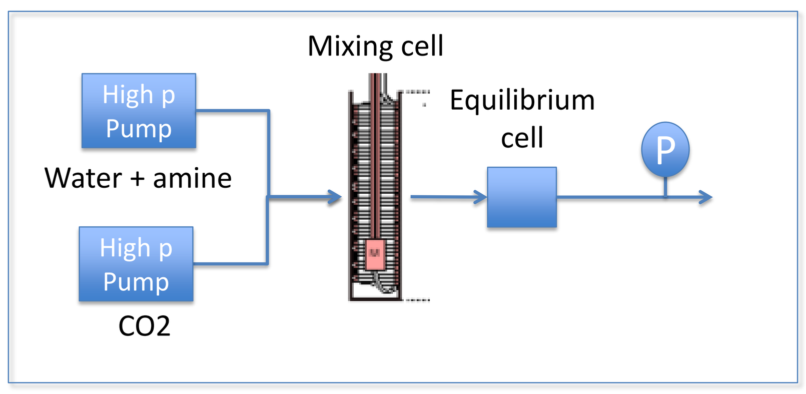
General overview





Below temperature of demixion | Above temperature of demixion

General design for both apparatuses

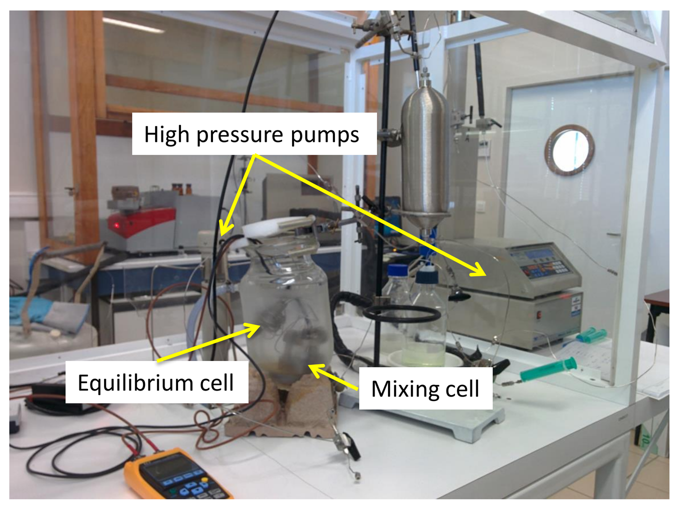


Comparison of the apparatuses

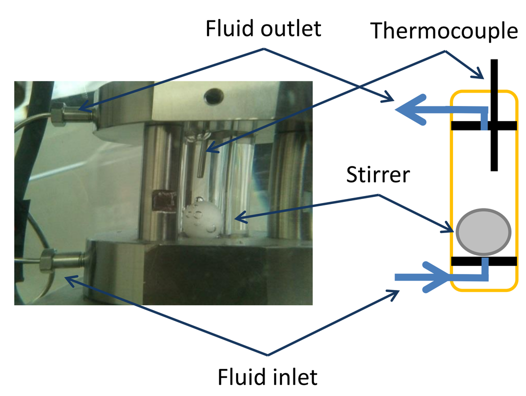
	Hastelloy cell	Sapphire cell
Temperature T	Room T – 428 K	263 – 423 K
Control of T	Heat tape	Thermostatic bath
Pressure p	0.1 – 40 MPa	0.1 – 8 MPa
Control of p	Buffer volume	Buffer volume
Volume of the cell	15 to 20 mL adjustable	5 mL
Visualization of the sample	Through the sapphire window	Full sample

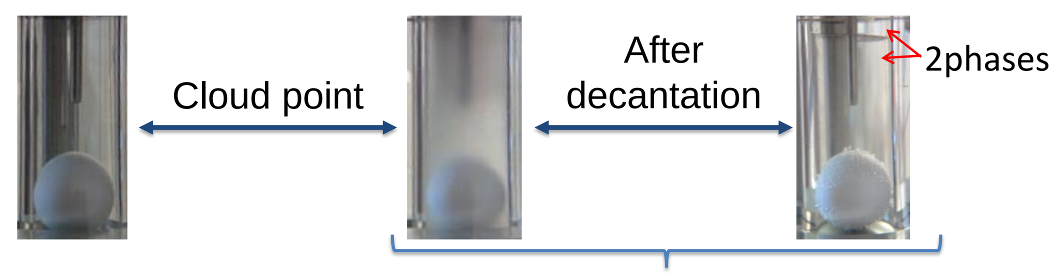
Sapphire Cell

General overview



Equilibrium cell



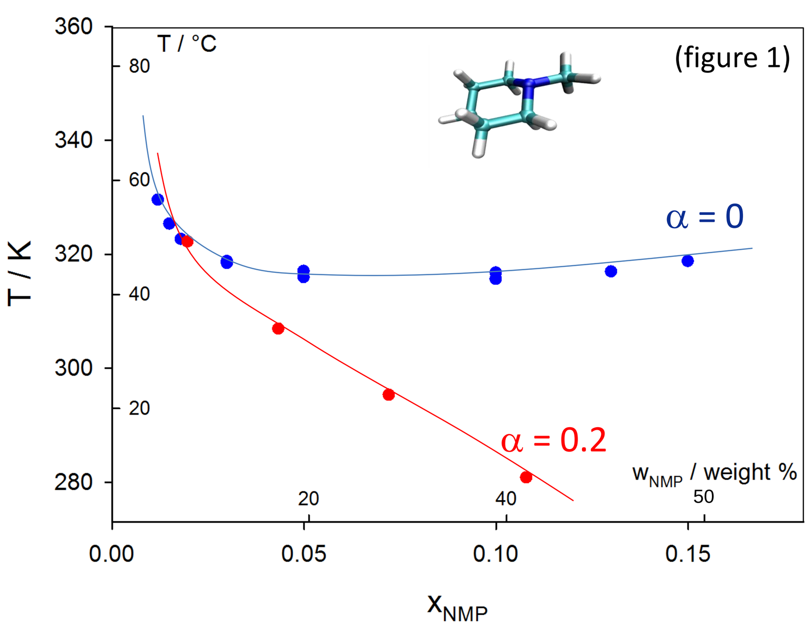


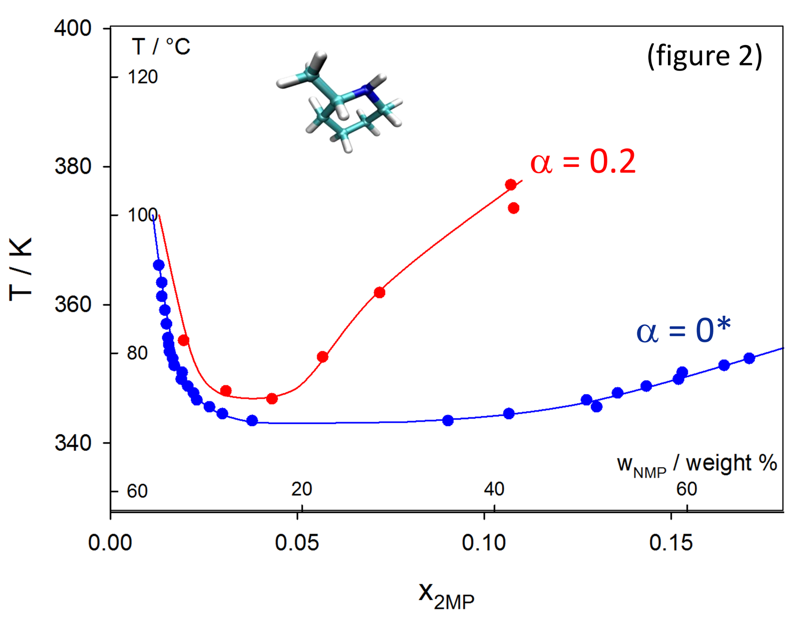
Below temperature of demixion | Above temperature of demixion

Results and Conclusions

Constant loading charge

Temperatures of liquid-liquid phase separation for solutions of water + N-methylpiperidine (NMP) + CO_2 (figure 1) and for solutions of water + 2-methylpiperidine (2MP) + CO_2 (figure 2) versus composition of the binary mixture water + methylpiperidine at different loading charges α. For 2MP, data at α = 0 are from reference [5]

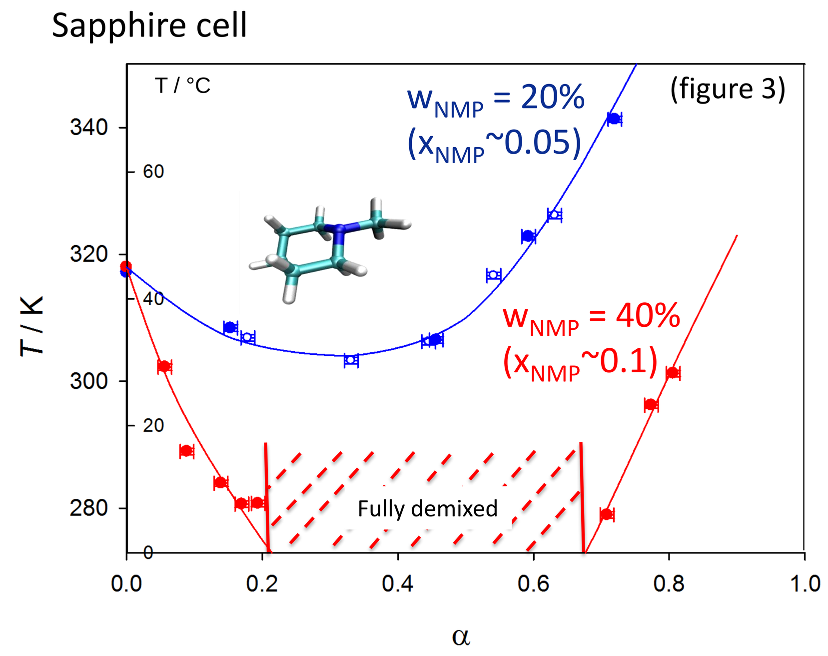


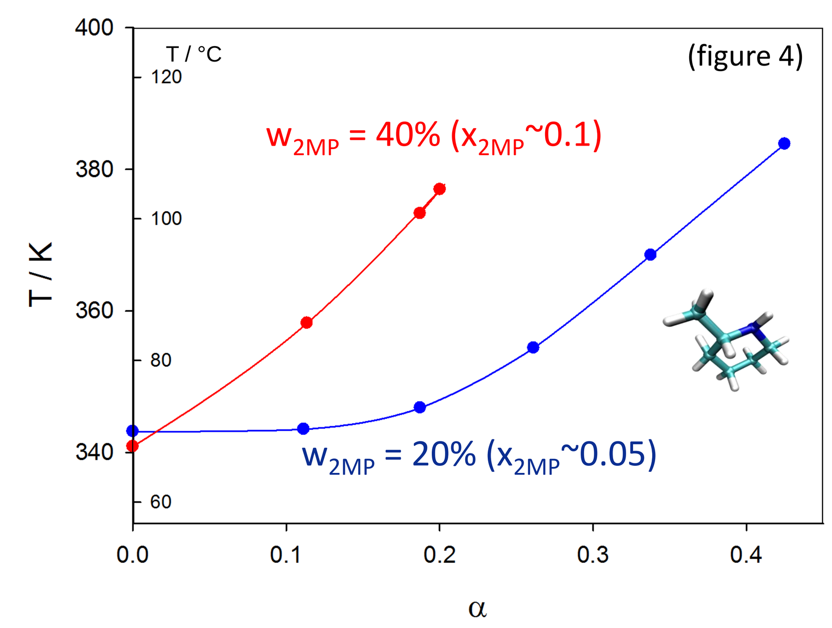


- Measurements were realized at 5 bar. Ternary mixtures are prepared below the temperature of liquid-liquid phase separation.
- Uncertainties
  - composition : $\begin{cases} \alpha : \pm 0.01 \\ x : \pm 0.001 \end{cases}$
  - Pressure : ± 0.1 bar , - Temperature : ± 0.3 K

Constant amine-water composition

Temperatures of liquid-liquid phase separation for solutions of water + N-methylpiperidine (NMP) + CO_2 (figure 3) and for solutions of water + 2-methylpiperidine (2MP) + CO_2 (figure 4) versus loading charge α at different compositions of the binary mixture water + methylpiperidine. Open symbols : Thar Inst. Cell; full symbol : Sapphire cell





	Water + amine	Water + amine + CO_2 (α = 0.2)	Water + amine + CO_2 (x = 0.05)
2-methylpiperidine	LCST = 341 K x = 0.07	LCST = 343 K x = 0.04	--------
N-methylpiperidine	LCST = 318 K x = 0.07	---------	LCST = 303 K α = 0.33

- Good agreement between the two methods
- LCST is strongly influenced by the presence of the dissolved gas
- N-methylpiperidine cannot be used in a process at high concentration (40%wt) as the CO_2 drastically lowered the LCST; 2-methylpiperidine is a better candidate.

ANR – NSERC joint program DACOOTA

The objective of the project, co-supported by ANR in France and NSERC in Canada, is to analyze the structure-properties relationships for different substituted piperidines.

Thermodynamic properties (enthalpies, heat capacities, volumes, phase equilibriums) are measured in Clermont-Ferrand (France). [6]
Speciation in solution using Raman spectroscopy at high temperature and pressure are determined in Guelph (canada).

Modeling using activity coefficient models and molecular simulation will complete the program.

References

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[5] Stephenson, J. Chem. Eng. Data, 38, 428 (1993)
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